

BIODEGRADABLE COMPOSITION, SHAPED ARTICLE OBTAINED THEREFROM AND METHOD OF PRODUCING BIODEGRADABLE MATERIAL

Patent number: GB2246355
Publication date: 1992-01-29
Inventor: NISHIYAMA MASASHI; HOSOKAWA JUN;
YOSHIHARA KAZUTOSHI; KUBO TAKAMASA;
KANAOKA KUNIO; KONDO KAZUO; MARUYAMA
SATOSHI; TATEISHI KENJI; UEDA AKIHIKO
Applicant: AGENCY IND SCIENCE TECHN (JP); OKURA
INDUSTRIAL CO LTD (JP)
Classification:
- **international:** B32B23/02; B32B27/04; B32B27/30; B32B27/36;
B32B27/40; C08L1/02; C08L5/08
- **european:** C08L67/00; C08L71/02; C08L75/04; C08L77/00;
C08L101/00
Application number: GB19910014019 19910628
Priority number(s): JP19910078584 19910318; JP19900170075 19900629

Also published as:

  FR2663942 (A)
 DE4121085 (A)

Report a data error he

Abstract not available for GB2246355

Data supplied from the **esp@cenet** database - Worldwide

(12) UK Patent Application (19) GB (11) 2 246 355⁽¹³⁾A

(43) Date of A publication 29.01.1992

(21) Application No 9114019.4

(22) Date of filing 28.06.1991

(30) Priority data

(31) 02170075
03078584

(32) 29.06.1990
18.03.1991

(33) JP

(71) Applicants

Director-General of Agency of Industrial Science and
Technology

(Incorporated in Japan)

1-3-1 Kasumigaseki, Chiyoda-ku, Tokyo, Japan

Okura Industrial Co Ltd

(Incorporated in Japan)

1515 Nakazu-cho, Marugame-shi, Kagawa-ken, Japan

(72) Inventors

Masashi Nishiyama

Jun Hosokawa

Kazutoshi Yoshihara

Takamasa Kubo

Kunio Kanaoka

Kazuo Kondo

Satoshi Maruyama

Kenji Tateishi

Akihiko Ueda

(51) INT CL⁵

C08L 1/02, B32B 23/02 27/04 27/30 27/36 27/40,
C08L 5/08

(52) UK CL (Edition K)

C3M MXC M101 M110 M112 M122 M125 M136
M153 M163 M163C M202
B2E EL E1538 E1729 E404S E429S E436S E439S
E443S E446S E456S E470S E489S
B5N N195 N196 N200 N207 N21Y N223 N225 N227
N2302 N2308 N237 N241 N244 N247 N255 N257
N2704 N2708 N2720 N2728 N273 N2730 N2734
N2736 N2740 N276 N278 N281 N283 N287 N37X
N372 N401 N402 N412 N413 N415 N416 N449
N46X N466 N478 N491 N501 N502 N518 N564
N57X N593 N595 N597 N601 N606 N615 N62X
N62Y N622 N627 N631 N637 N643 N645 N661
N668 N670 N673 N76X N78X
U1S S1012 S1700 S1814

(56) Documents cited

None

(58) Field of search

UK CL (Edition K) C3M MXC

INT CL⁵ C08L

Online: WPI

(74) Agent and/or Address for Service

Lloyd Wise, Tregear & Co

Norman House, 105-109 Strand, London, WC2R 0AE,
United Kingdom

(54) Biodegradable composition, shaped article obtained therefrom and method of producing biodegradable material

(57) A biodegradable film or the like shaped article is formed from a composition including 100 parts by weight of cellulose fibers having a length of 3 mm or less and a diameter of 50 μ m or less, 10-600 parts by weight of a thermoplastic resin and 2-100 parts by weight of chitosan. A mixture containing (a) an aqueous solution of an acid salt of chitosan, (b) an aqueous dispersion or solution of a thermoplastic resin and (c) fine cellulose fibers is dried and shaped to obtain such a biodegradable shaped article. A layer of a biodegradable material may be formed on at least one side of the film.

Chitosan is a product obtained by deacetylation of chitin contained in mycelia or crust of Crustacea such as crab or lobster.

GB 2 246 355 A

BIODEGRADABLE COMPOSITION, SHAPED ARTICLE OBTAINED
THEREFROM AND METHOD OF PRODUCING BIODEGRADABLE MATERIAL

Background of the Invention

This invention relates to a biodegradable composition and a shaped article formed from the composition. The present invention is also directed to
5 a method of producing a biodegradable material.

In view of the recent increasing problems of environmental pollution, the use of biodegradable plastics which are able to be decomposed by microorganisms when left in soil is being encouraged.

10 Japanese Published Unexamined Patent Application (Tokkyo Kokai) No. Hei-2-6689 discloses a biodegradable composite sheet composed of cellulose and chitosan. Though this composite sheet exhibits satisfactory biodegradability, it has been found that
15 the sheet involves a problem when used for industrial applications. Namely, this composite material is so stiff that utilization thereof is limited to specific applications. While it is possible to impart flexibility to such a composite sheet by incorporating a
20 plasticizer, such as glycerin, sorbitol, ethylene glycol or polyethylene glycol, thereinto, the resulting sheet is found to gradually lose the flexibility when kept in contact with water and then dried because the plasticizer dissolves into the water with time.

25 Summary of the Invention

There is provided in accordance with one aspect of the present invention a composition of matters, comprising 100 parts by weight of cellulose fibers having a length of 3 mm or less and a diameter of 50 μ m or less,
30 10-600 parts by weight of a thermoplastic resin and 2-100 parts by weight of chitosan.

In another aspect, the present invention provides a shaped article obtained from the above composition.

In a further aspect, the present invention
5 provides a composite film comprising a substrate film
formed of a biodegradable composition comprising 100
parts by weight of cellulose fibers having a length of
3 mm or less and a diameter of 50 μ m or less and 2-100
parts by weight of chitosan, and a layer provided at
10 least one side of said substrate film and formed of a
biodegradable material.

The present invention also provides a method of
producing a biodegradable material, comprising the steps
of:

15 providing (a) an aqueous solution of an acid
salt of chitosan and (b) an aqueous dispersion or
solution of a thermoplastic resin;

mixing cellulose fibers having a length of 3 mm
or less and a diameter of 50 μ m or less with said aqueous
20 solution (a) and said aqueous dispersion or solution (b)
to form a mixture; and

drying said mixture.

Particular preferred embodiments of the
invention allow the following objects, among others, to
25 be achieved:

to provide a biodegradable composition suitable
for forming into shaped articles;

to provide a composition of the above-mentioned
type which has good flexibility and is suited as a raw
30 material for the production of shaped articles,
especially films and sheets;

to provide a composition of the above-mentioned
type which has improved stability to water;

to provide a shaped article having a good
35 flexibility;

to provide a composite sheet or film which has
good heat-sealability.

The chitosan and the cellulose fibers in the above composition may be present in the form of a composite in which they are bonded to each other. The bonding may include chemical bonding between the amino
5 groups of the chitosan and the carbonyl groups of the cellulose fibers.

In the present specification and appended claims, the term "shaped article" is intended to refer to powders, films, sheets, coatings, mats, plates, blocks
10 and the like shaped bodies and composite articles using these materials.

Other objects, features and advantages of the present

invention will become apparent from the detailed description of the preferred embodiments of the invention to follow.

Detailed Description of the Preferred
Embodiments of the Invention

5 The biodegradable composition according to the present invention includes cellulose fibers, chitosan and a thermoplastic resin.

10 Any cellulose fiber may be used for the purpose of the present invention. Examples of suitable cellulose fibers include fibers formed of cellulose, hemicellulose or lignocellulose obtained from wood, straw, cotton, jute, bamboo or bagasse and cellulose produced by bacteria. Beaten fibers with a length of 3 mm or less, preferably 1 mm or less and a
15 diameter of 50 μ m or less, preferably 30 μ m or less are suitably used in the present invention.

 Chitosan is a product obtained by deacetylation of chitin contained in mycelia or crust of Crustacea such as crab or lobster. The molecular weight and deacetylation degree of
20 chitosan to be used in the present invention are not specifically limited. However, a deacetylation degree of at least 60 % is desired for reasons of increased solubility.

 Any thermoplastic resin may be used in the present invention, though biodegradable and/or water-insoluble one is
25 preferred. Examples of suitable biodegradable thermoplastic resins include polyvinyl alcohols, polyurethanes obtained by reaction of a polyester polyol with a diisocyanate, polyurethanes obtained by reaction of a polyester polyol and a polyether polyol with a diisocyanate, polyethylene oxides and
30 aliphatic polyesters. As the aliphatic polyester, poly- ϵ -caprolactone is especially preferably used. Examples of suitable water-insoluble thermoplastic resins include polyurethanes, polyacrylates, polyvinyl acetates, polyamides and polyesters.

35 The use of the above-exemplified thermoplastic resins is preferable also because they show good compatibility with

cellulose fibers and chitosan. From the standpoint of biodegradability, stability to water, compatibility with both cellulose fibers and chitosan and flexibility, the use of polyurethanes obtained by reaction of a polyester polyol with a diisocyanate or reaction of a polyester polyol and a polyether polyol with a diisocyanate is particularly preferred.

The amount of the chitosan is 2-100 parts by weight, preferably 5-80 parts by weight, per 100 parts by weight of the cellulose fibers, while the amount of the thermoplastic resin is 10-600 parts by weight, preferably 20-400 parts by weight, per 100 part by weight of the cellulose fibers. An amount of the chitosan outside the above range is undesirable because the wet strength becomes low. An amount of the thermoplastic resin below 10 parts by weight is insufficient to impart desired flexibility. On the other hand, too large an amount of the thermoplastic resin causes reduction of biodegradability of the composition.

One preferred method for the preparation of a biodegradable material includes the steps of:

providing (a) an aqueous solution of an acid salt of chitosan and (b) an aqueous dispersion or solution of the above thermoplastic resin;

mixing the above-described cellulose fibers having a length of 3 mm or less and a diameter of 50 μ m or less with the aqueous solution (a) and the aqueous dispersion or solution (b) to form a mixture; and

drying the mixture.

By shaping the mixture into a desired form before the drying, there is obtainable a biodegradable shaped article according to the present invention. For example, by spreading the mixture on a suitable surface such as of a glass plate, a shaped article in the form of a film may be obtained.

In performing the above method, since chitosan as such is not soluble in water, it is advisable to use chitosan in the form of an acid salt, such as hydrochloride or the like inorganic acid salt or formate, acetate, lactate or the like organic acid salt.

The mixture may further contain one or more additives such as a filler and a colorant. Both organic filler such as starch and inorganic filler such as silica may be used. The drying step may be performed at room temperature or an elevated temperature of up to 200 °C, preferably in the range of 50-160 °C.

In one preferred embodiment, the above composition may be used for forming a substrate of a composite film having a biodegradable thermoplastic layer formed on at least one side of the substrate. The composite film shows good heat-sealability so that it is suitably used as packaging films or as construction sheets for green houses.

The thermoplastic resin contained in the substrate is preferably is a biodegradable one such as exemplified previously. The biodegradable thermoplastic layer or layers to be provided on one or both sides of the substrate may be formed of a material selected from polyvinyl alcohols, polyurethanes obtained by reaction of a polyester polyol with a diisocyanate, polyurethanes obtained by reaction of a polyester polyol and a polyether polyol with a diisocyanate, polyethylene oxides and aliphatic polyesters. Because of the presence of the thermoplastic resin in the substrate, the biodegradable layer has good compatibility with the substrate so that tight bonding may be established therebetween.

The layer of the biodegradable thermoplastic material may be provided on the substrate by any suitable method such as by coating a solution or a melt of the biodegradable material on the substrate or by bonding a film of the biodegradable material with the substrate. The bonding may be effected by fuse-bonding or with the use of an adhesive. The thickness of the biodegradable layer is preferably 1-20 µm.

In the above composite film, if the heat sealability only is desired and the tight bonding between the substrate and the biodegradable layer is not important, then the thermoplastic resin may be removed from the constituents of the substrate.

The following examples will further illustrate the present invention.

The test methods used in the examples are as follows:

Tensile Strength:

5 Tensile strength is measured in accordance with ASTM D882-81.

Wet Strength:

10 Sample film is immersed in water at 23 °C for 24 hours. The tensile strength of the resulting film is then measured.

Stiffness:

15 A film stiffness tester is used for measuring the stiffness of sample film with a width of 15 mm and a thickness of 90 µm.

Stability to Water:

20 Sample film is immersed in water at 23 °C for 24 hours and then dried. Stability to water is evaluated in terms of weight loss which is calculated as follows:

$$\text{Weight Loss (\%)} = (W_0 - W_1) / W_0 \times 100$$

wherein W_0 is the weight of the sample before immersion into water and W_1 is the weight of the sample after immersion.

25 Biodegradability:

30 Sample film is buried in soil contained in a polyethylene vessel. This is maintained at a temperature of 23 °C and a relative humidity of 95-100 % for 3 months. The soil is then removed to observe the state of the sample.

Seal Strength:

35 Two sample films are heat-bonded by means of an impulse sealing device and cut into a width of 10 mm. The bonded films are drawn at a drawing speed of 300 mm/minute to measure the rupture strength required for breaking the bonding.

Example 1

Bleached pulp from needle-leaved tree was dispersed in water and subjected to a beating treatment to obtain a dispersion containing 1 % by weight of cellulose fibers with a length of 0.5 mm or less and a diameter of 0.1 μ m or less. The dispersion was then mixed with quantities of an aqueous solution containing 1 % by weight of an acetic acid salt of chitosan and an aqueous dispersion of polyurethane (SUPERFLEX 300 manufactured by Daiichi Kogyo Seiyaku K. K., solid content: 30 % by weight) to obtain a mixture having chitosan salt and polyurethane contents of 20 parts by weight and 75 parts by weight, respectively, per 100 parts by weight of the cellulose fibers. The mixture was spread over the surface of a glass plate and dried under a hot air stream at 70 °C for 6 hours to obtain a translucent film. The biodegradability test revealed that this film was decomposed so that the original shape was completely destroyed. The film was further tested for its tensile strength, stiffness and stability to give the results shown in Table 1.

Examples 2-5

Example 1 was repeated in the same manner as described except that SUPERFLEX 300 was replaced by a forcedly-emulsified type polyurethane aqueous dispersion (SUPERFLEX E2000 manufactured by Daiichi Kogyo Seiyaku K. K., solid content: 25 % by weight) in Example 2, by a polyester-type polyurethane resin emulsion (YODOSOL GC52, manufactured by Kanebo NSC K. K., solid content: 50 % by weight) in Example 3, by an acrylate copolymer latex (NACRYLIC 125-4445, manufactured by Kanebo NSC K. K., solid content: 35 % by weight) in Example 4 and by a polyvinyl acetate emulsion (solid content: 41 % by weight) in Example 5. The biodegradability test revealed that each of the films thus obtained was decomposed so that the original shape was completely destroyed. The tensile strength, stiffness and stability of each of the films are shown in Table 1.

Comparative Examples 1-4

Example 1 was repeated in the same manner as described except that SUPERFLEX 300 was replaced by glycerin in Comparative Example 1, by sorbitol in Comparative Example 2, by trimethylol propane in Comparative Example 3 and polyethylene glycol (#200) in Comparative Example 4.

Table 1

10

Example No.	Dry Tensile Strength (kg/cm ²)	Wet Tensile Strength (kg/cm ²)	Stiff- ness (g)	Weight Loss (%)	
15	1	987	520	10.4	5.6
	2	1084	483	7.3	2.7
	3	845	306	11.4	2.7
	4	840	369	9.2	1.9
	5	928	214	13.4	5.3
20	Comptv. 1	715	533	4.4	35.3
	Comptv. 2	887	478	5.5	36.6
	Comptv. 3	837	467	8.3	32.2
	Comptv. 4	778	457	7.2	33.0

Example 6-15 and Comparative Examples 5-7

Bleached pulp from needle-leaved tree was dispersed in water and subjected to a beating treatment to obtain a dispersion containing 1 % by weight of cellulose fibers with a length of 0.5 mm or less and a diameter of 0.1 μ m or less. The dispersion was then mixed with quantities of an aqueous solution containing 1 % by weight of an acetic acid salt of chitosan and the resin shown in Table 2 to obtain a mixture having chitosan salt and resin contents as shown in Table 2 per 100 parts by weight of the cellulose fibers. The mixture was spread over the surface of a glass plate and dried under a hot air stream at 70 °C for 6 hours to obtain translucent films. The biodegradability test revealed that each of the films was

decomposed so that the original shape was completely destroyed. The films were further tested for their tensile strength, stiffness and stability to give the results shown in Table 2.

5

Table 2

Example No.	Amount of Chito-san (part)	Resin Kind	Amount (part)	Dry Tensile Strength (kg/cm ²)	Wet Tensile Strength (kg/cm ²)	Stiffness (g)	Weight Loss (%)
10	20	*1	25	1215	468	17.2	2.3
	20	*1	50	1138	533	13.8	4.5
	20	*1	100	852	443	10.9	5.8
15	20	*1	150	575	330	7.1	6.9
	20	*1	200	437	258	3.6	5.9
	20	*2	100	892	422	12.9	3.0
	20	*3	200	498	255	7.4	2.8
	20	*4	75				
20		*5	75	654	225	12.3	7.7
	5	*1	300	229	115	1.5	7.1
	50	*3	100	593	150	5.5	2.1
	Comp.5	-	-	1537	627	27.5	3.3
	Comp.6	-	-	1458	345	23.0	1.1
25	Comp.7	-	-	1218	146	20.0	5.8

*1: Aqueous dispersion of polyurethane (SUPERFLEX 300, obtained by reaction of a polyester polyol and a polyether polyol with a diisocyanate, manufactured by Daiichi Kogyo Seiyaku K. K., solid content: 30 % by weight)

*2: Forcedly-emulsified type polyurethane aqueous dispersion (SUPERFLEX E2000 manufactured by Daiichi Kogyo Seiyaku K. K., solid content: 25 % by weight)

*3: Polyester-type polyurethane resin emulsion (YODOSOL GC52, manufactured by Kanebo NSC K. K., solid content: 50 % by weight)

*4: Acrylate copolymer latex (NACRYLIC 125-4445,
manufactured by Kanebo NSC K. K., solid content: 35 %
by weight)

*5: Polyvinyl alcohol

5 Example 16

An aqueous dispersion containing 1 % by weight of
cellulose fibers was mixed with quantities of an aqueous
solution containing 1 % by weight of an acetic acid salt of
chitosan and an aqueous dispersion of polyurethane (SUPERFLEX
10 300 manufactured by Daiichi Kogyo Seiyaku K. K., solid content:
30 % by weight) to obtain a mixture having chitosan salt and
polyurethane contents of 20 parts by weight and 100 parts by
weight, respectively, per 100 parts by weight of the cellulose
fibers. The mixture was spread over the surface of a glass
15 plate and dried under a hot air stream at 70 °C to obtain a
translucent film with a thickness of 80 µm. A 20 % by weight
solution of a poly-ε-caprolactone in ethyl acetate was then
applied on the thus obtained substrate film by means of a bar
coater and the coating was dried at 50 °C to obtain a composite
20 film having a poly-ε-caprolactone layer with a thickness of 3
µm. The biodegradability test revealed that the composite film
was completely decomposed. The composite film showed a seal
strength of 1135 g/10 mm.

25 Example 17

An aqueous dispersion containing 1 % by weight of
cellulose fibers was mixed with quantities of an aqueous
solution containing 1 % by weight of an acetic acid salt of
chitosan and an aqueous dispersion of polyurethane (SUPERFLEX
30 300 manufactured by Daiichi Kogyo Seiyaku K. K., solid content:
30 % by weight) to obtain a mixture having chitosan salt and
polyurethane contents of 20 parts by weight and 50 parts by
weight, respectively, per 100 parts by weight of the cellulose
fibers. The mixture was spread over the surface of a glass
35 plate and dried under a hot air stream at 70 °C to obtain a
translucent film with a thickness of 80 µm. A 10 % by weight

solution of a polyurethane, obtained from a polyester polyol, in tetrahydrofran was then applied on the thus obtained substrate film by means of a bar coater and the coating was dried at 50° C to obtain a composite film having a polyurethane layer with a thickness of 9 µm. The biodegradability test revealed that the composite film was completely decomposed. The composite film showed a seal strength of 907 g/10 mm.

Example 18

Example 17 was repeated in the same manner as described except that the content of the polyurethane in the substrate film was increased to 150 parts by weight per 100 parts by weight of the cellulose fibers. The biodegradability test revealed that the composite film was almost completely decomposed. The composite film showed a seal strength of 1313 g/10 mm.

Example 19

An aqueous dispersion containing 1 % by weight of cellulose fibers was mixed with quantities of an aqueous solution containing 1 % by weight of an acetic acid salt of chitosan, an aqueous solution of polyethylene oxide and glycerin to obtain a mixture having a chitosan salt content of 20 parts by weight, a polyethylene oxide content of 100 parts by weight and a glycerin content of 75 parts by weight per 100 parts by weight of the cellulose fibers. The mixture was spread over the surface of a glass plate and dried under a hot air stream at 70 °C to obtain a translucent film with a thickness of 80 µm. A 10 % by weight aqueous solution of a polyethylene oxide was then applied on the thus obtained substrate film by means of a bar coater and the coating was dried at 50 °C to obtain a composite film having a polyethyleneoxide layer with a thickness of 15 µm. The biodegradability test revealed that the composite film was almost completely decomposed. The composite film showed a seal strength of 1220 g/10 mm.

Example 20

Chitosan (1 part by weight) was mixed with 98 parts by weight of water and 1 part by weight of acetic acid to obtain an aqueous solution of chitosan acetate. This solution (28 parts
5 by weight) was then mixed with 140 parts by weight of aqueous dispersion containing 1 % by weight of fine cellulose fibers and 1.05 parts by weight of glycerin and the mixture was applied onto a glass plate and dried at 70° C, thereby obtaining a substrate film with a thickness of 70 μ m. A 20 % by weight
10 solution of a poly- ϵ -caprolactone in ethyl acetate was then applied on the thus obtained substrate film by means of a bar coater and the coating was dried at 50° C to obtain a composite film having a poly- ϵ -caprolactone layer with a thickness of 3 μ m. The biodegradability test revealed that the composite film
15 was completely decomposed. The composite film showed a seal strength of 33 g/10 mm.

Example 21

Example 20 was repeated in the same manner as
20 described except that the poly- ϵ -caprolactone layer had a thickness of 9 μ m. The biodegradability test revealed that the composite film was completely decomposed. The composite film showed a seal strength of 145 g/10 mm.

25 Example 22

Example 20 was repeated in the same manner as described except that the poly- ϵ -caprolactone layer had a thickness of 15 μ m. The biodegradability test revealed that the composite film was completely decomposed. The composite film
30 showed a seal strength of 303 g/10 mm.

Example 23

A substrate film similar to that of Example 20 was applied with a 10 % by weight solution of polyester-type
35 polyurethane in tetrahydrofuran and the coating was dried at 50° C for 5 minutes to form a polyurethane layer with a thickness of 9 μ m on the substrate film. The biodegradability test

revealed that the composite film was almost completely decomposed. The composite film showed a seal strength of 130 g/10 mm.

5 Example 24

A substrate film similar to that of Example 20 was applied with a 10 % by weight aqueous solution of polyethylene oxide and the coating was dried at 50 ° C for 5 minutes to form a polyethylene oxide layer with a thickness of 9 µm on the
10 substrate film. The biodegradability test revealed that the composite film was completely decomposed. The composite film showed a seal strength of 80 g/10 mm.

Example 25

15 An aqueous dispersion containing 1 % by weight of cellulose fibers was mixed with a quantity of an aqueous solution containing 1 % by weight of an acetic acid salt of chitosan to obtain a mixture having a chitosan salt content of
20 20 parts by weight per 100 parts by weight of the cellulose fibers. The mixture was spread over the surface of a glass plate and dried under a hot air stream at 70 ° C to obtain a translucent film with a thickness of 80 µm. A 20 % by weight
25 solution of a poly-ε-caprolactone in ethyl acetate was then applied on the thus obtained substrate film by means of a bar coater and the coating was dried at 50 ° C to obtain a composite film having a poly-ε-caprolactone layer with a thickness of 3
µm. The biodegradability test revealed that the composite film was completely decomposed. The composite film showed a seal strength of 39 g/10 mm.

30

Example 26

A substrate film similar to that of Example 25 was applied with a 10 % by weight solution of polyester-type polyurethane in tetrahydrofuran and the coating was dried at 50
35 ° C for 5 minutes to form a polyurethane layer with a thickness of 9 µm on the substrate film. The biodegradability test revealed that the composite film was almost completely

decomposed. The composite film showed a seal strength of 158 g/10 mm.

The invention may be embodied in other specific forms without departing from the spirit or essential
5 characteristics thereof. The present embodiments are therefore to be considered in all respects as illustrative and not restrictive, the scope of the invention being indicated by the appended claims rather than by the foregoing description, and all the changes
10 which come within the meaning and range of equivalency of the claims are therefore intended to be embraced therein.

WHAT IS CLAIMED IS:

1. A composition of matters, comprising 100 parts by weight of cellulose fibers having a length of 3 mm or less and a diameter of 50 μ m or less, 10-600 parts by weight of a thermoplastic resin and 2-100 parts by weight of chitosan.

2. A composition as set forth in claim 1, wherein said thermoplastic resin is biodegradable.

3. A composition as set forth in claim 2, wherein said thermoplastic resin is at least one member selected from the group consisting of polyvinyl alcohols, polyurethanes obtained by reaction of a polyester polyol with a diisocyanate,
5 polyurethanes obtained by reaction of a polyester polyol and a polyether polyol with a diisocyanate, polyethylene oxides and aliphatic polyesters.

4. A composition as set forth in claim 1, wherein said thermoplastic resin is substantially insoluble in water.

5. A composition as set forth in claim 4, wherein said thermoplastic resin is at least one member selected from the group consisting of polyurethanes, polyacrylates, polyvinyl acetates, polyamides and polyesters.

6. A composition as set forth in claim 4, wherein said thermoplastic resin is biodegradable.

7. A composition as set forth in claim 6, wherein said thermoplastic resin is at least one member selected from the group consisting of polyurethanes obtained by reaction of a

polyester polyol with a diisocyanate and polyurethanes obtained
5 by reaction of a polyester polyol and a polyether polyol with a
diisocyanate.

8. A shaped article formed from the composition according
to claim 1.

9. A shaped article as set forth in claim 8, comprising a
substrate film formed of said composition and a layer provided
at least one side of said substrate film and formed of a
biodegradable material.

10. A shaped article as set forth in claim 9, wherein said
thermoplastic resin is biodegradable.

11. A shaped article as set forth in claim 10, wherein said
thermoplastic resin is at least one member selected from the
group consisting of polyvinyl alcohols, polyurethanes obtained
by reaction of a polyester polyol with a diisocyanate,
5 polyurethanes obtained by reaction of a polyester polyol and a
polyether polyol with a diisocyanate, polyethylene oxides and
aliphatic polyesters.

12. A shaped article as set forth in claim 9, wherein said
biodegradable material is at least one member selected from the
group consisting of polyvinyl alcohols, polyurethanes obtained
by reaction of a polyester polyol with a diisocyanate,
5 polyurethanes obtained by reaction of a polyester polyol and a
polyether polyol with a diisocyanate, polyethylene oxides and
aliphatic polyesters.

13. A composite film comprising a substrate film formed of a biodegradable composition comprising 100 parts by weight of cellulose fibers having a length of 3 mm or less and a diameter of 50 μ m or less and 2-100 parts by weight of chitosan, and a layer provided at least one side of said substrate film and formed of a biodegradable material.

14. A composite film as set forth in Claim 13, wherein said biodegradable material is at least one member selected from the group consisting of polyvinyl alcohols, polyurethanes obtained by reaction of a polyester polyol with a diisocyanate, polyurethanes obtained by reaction of a polyester polyol and a polyether polyol with a diisocyanate, polyethylene oxides and aliphatic polyesters.

15. A method of producing a biodegradable material, comprising the steps of:

providing (a) an aqueous solution of an acid salt of chitosan and (b) an aqueous dispersion or solution of a thermoplastic resin;

mixing cellulose fibers having a length of 3 mm or less and a diameter of 50 μ m or less with said aqueous solution (a) and said aqueous dispersion or solution (b) to form a mixture; and

drying said mixture.

16. A composition substantially as hereinbefore described with reference to the Examples.

17. A composite film substantially as hereinbefore described with reference to the Examples.

18. A method of producing a biodegradable material substantially as hereinbefore described, with reference to the Examples.